

**Amendments to the Specification:**

**Please replace the paragraph on page 1, lines 8-13, with the following amended paragraph:**

The present invention (a first aspect of the present invention) relates to a production method ~~of~~ for a DDR type zeolite membrane. More particularly, the present invention relates to a method for easily producing a DDR type zeolite membrane having an industrially acceptable thickness in a short period of time.

**Please replace the paragraph on page 3, lines 3-13, with the following amended paragraph:**

There have been proposed only a few production methods for such DDR type zeolites. Some proposals have been made on powder synthesis, but no proposals have been made on the synthesis of the membrane. As ~~a one of the few proposals related to powder related technique of the powder synthesis that is one of the few proposals~~, for example, M. J. den Exter, J. C. Jansen, H. van Bekkum, Studies in Surface Science and Catalysis vol. 84, Ed. by J. Weitkamp et. al., Elsevier (1994) 1159-1166 discloses a method for producing a DDR type zeolite powder by hydrothermal synthesis using tetramethoxysilane, 1-adamantanamine, ethylenediamine, or the like, as raw materials.

**Please replace the paragraphs on page 3, line 19 – page 4, line2, with the following amended paragraphs:**

Further, this production method provides only a DDR type zeolite powder with a crystal size of 5 to 25  $\mu\text{m}$ , and thus has a problem that it cannot produce a dense separation membrane having a sufficient thickness for a gas separation process in a petrochemical industry or the like.

The present invention (a first aspect of the present invention) is made in view of the problems of the related art, and has an object to provide a method for easily

producing a DDR type zeolite membrane having a thickness that is acceptable in an industrial gas separation process or the like and in a short period of time.

**Please replace the paragraphs on page 5, line 16 – page 6, line 23, with the following amended paragraphs:**

Thus, Vroon et al. of University of Twente propose that the defects such as cracks can be effectively prevented by making the thickness of the zeolite membrane to be formed on an alumina substrate thinner (See Journal of Membrane Science 144 (1998) 65-76). However, the probability in the occurrence of defects such as cracks due to thermal stress can not be reduced sufficiently by simply making the zeolite membrane thinner.

There ~~are~~ is disclosed in JP-A-9-202615 a zeolite membrane having a zeolite crystal ~~in~~ on a porous substrate and a production method of the same. It describes that the occurrence of defects such as cracks due to thermal stress in the thermal treatment process of the zeolite membrane and the like can be reduced by employing such a constitution that a porous substrate possesses zeolite crystal in the inside thereof.

However, there is a problem that the zeolite membranes disclosed in JP-A-9-202615 and the like can not ~~be~~ always be applicable to all types of zeolites. For example, for an LTA type zeolite, defects such as cracks of a zeolite membrane formed on a porous substrate cannot be decreased. The above described advantage varies, depending upon materials of the porous substrate, and for example, when alumina is used for a porous substrate, and an MFI type zeolite is used for a zeolite membrane, the defects such as cracks or the like occur ~~with the use of~~ after the zeolite membrane ~~only for several~~ is used a few times.

Incidentally, in the case of the zeolite membrane disclosed in JP-A-9-202615, a porous substrate of 0.5 mm or more in thickness is used since an amount of raw material solution being present in the porous substrate is important. If a zeolite membrane composite thus configured is too thick when used as a gas separation membrane, there is such a problem that pressure loss becomes large, thereby a sufficient gas flux can not be attained.

**Please replace the heading on page 7, line 5, with the following amended heading:**

~~Disclosure~~ Summary of the Invention

**Please replace the paragraph on page 14, lines 9-21, with the following amended paragraph:**

As described above, a DDR type zeolite membrane of the present invention (the second aspect of the present invention) may separate at least one type of particular gas components from a mixed gas containing at least ~~least~~ least two types of particular gas components such as a natural gas since its respective single gas permeances of at least two kinds of gases selected from the group consisting of a plurality of the particular gases are different from each other. Since it is formed on the substrate, it has a high mechanical strength. And, since it is a DDR type zeolite membrane (an inorganic substance), it shows a high heat resistance, and can prevent plasticization caused by carbon dioxide, and deterioration by liquid hydrocarbon.

**Please replace the paragraph on page 15, line 22 – page 16, line 2, with the following amended paragraph:**

In a DDR type zeolite membrane composite according to the present invention (the third aspect of the present invention), it is preferable that the a-DDR type zeolite membrane composite further comprises a DDR type zeolite layer deposited outside of the substrate, which is made of a DDR type zeolite and has a thickness of 30  $\mu\text{m}$  or less, on a surface of the porous substrate on which the DDR type zeolite layer deposited within pores of substrate is disposed.

**Please replace the paragraph on page 17, lines 3-7, with the following amended paragraph:**

In the production method of a DDR type zeolite membrane composite according to the present invention (the third aspect of the present invention), it is preferable to use a porous substrate that has a mean pore diameter of 0.05 to 10  $\mu\text{m}$  as ~~said-the~~ porous substrate.

**Please replace the heading on page 19, line 23, with the following amended heading:**

~~Best Mode for Carrying out~~ Detailed Description of the Invention

**Please replace the paragraph on page 26, lines 23-25, with the following amended paragraph:**

~~Now, embodiments of the present invention (a~~ A ~~second aspect of the present invention)~~ will now be described in detail with reference to the drawings.

**Please replace the paragraph on page 28, lines 7-13, with the following amended paragraph:**

"Porous" means, for example, having many three-dimensionally communicated ~~many~~ micropores, and a pore diameter is preferably 0.003 to 10  $\mu\text{m}$ , and more preferably 0.005 to 5  $\mu\text{m}$ . A diameter below 0.003  $\mu\text{m}$  causes high resistance when a gas permeates, and a diameter exceeding 10  $\mu\text{m}$  tends to cause a pin-hole in a DDR type zeolite membrane, which are not preferable.

**Please replace the paragraph on page 29, lines 7-18, with the following amended paragraph:**

Since it has the different gas permeances as to the above-mentioned particular gases (carbon dioxide, hydrogen, oxygen, nitrogen, water vapor, methane, normal butane, isobutane, sulfur hexafluoride, ethane, ethylene, propane, propylene, carbon monoxide, and nitrogen monoxide), as is discussed above, one or more types of particular gas components may be separated from a mixed gas containing two or more particular gas components such as a natural gas. This DDR type zeolite membrane has high heat resistance, and the plasticization caused by carbon dioxide and the deterioration by liquid hydrocarbon hardly occur, which is not the case when likely the membrane is composed of an organic substance.

**Please replace the paragraph on page 34, lines 18-26, with the following amended paragraph:**

One may separate effectively said at least one type of gas by using this DDR type zeolite membrane according to the embodiment, since it has different single gas permeances, respectively at room temperature and 100°C among at least two types of gases ~~selected from~~ selected from a group consisting of carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), water (H<sub>2</sub>O), methane (CH<sub>4</sub>), normal butane (n-C<sub>4</sub>H<sub>10</sub>), isobutane (i-C<sub>4</sub>H<sub>10</sub>), sulfur hexafluoride (SF<sub>6</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), propane (C<sub>3</sub>H<sub>8</sub>), and propylene (C<sub>3</sub>H<sub>6</sub>).

**Please replace the paragraph on page 39, lines 3-5, with the following amended paragraph:**

~~Now, embodiments of the present invention (a~~ A ~~third aspect of the present invention)~~ will now be described in detail with reference to the drawings.

**Please replace the paragraph on page 40, line 26 – page 41, line 14, with the following amended paragraph:**

A forming method of a DDR type zeolite layer deposited outside of the substrate 304 according to the embodiment is not limited, for example, a DDR type zeolite layer deposited outside of the substrate 304 can be formed by immersing the porous substrate 302 in a raw material solution used for forming a DDR type zeolite to perform hydrothermal synthesis. When the porous substrate 302 is immersed in the raw material solution, the pores 303 of the porous substrate 302 is-are impregnated with the raw material solution to form the DDR type zeolite layer deposited within pores of substrate 305. At this time, using a raw material solution having a relatively high concentration within a range of a raw material solution used in forming a DDR type zeolite can facilitate forming the DDR type zeolite layer deposited within pores of substrate 305 within the pores 303 of the porous substrate 302.

**Please replace the paragraph on page 42, line 26 – page 43, line 13, with the following amended paragraph:**

Next, an embodiment of a production method of a DDR type zeolite membrane composite according to the present invention (the third aspect of the present invention) will be described. The production method of a DDR type zeolite membrane composite according to the embodiment is characterized by forming a raw material solution having a mixing ratio of 1-adamantanamine to silica (1-adamantanamine (mol)/silica (mol)) of 0.03 to 0.4, and a mixing ratio of water to silica (water (mol)/SiO<sub>2</sub> (mol)) of 20 to 500, immersing a porous substrate in thus formed raw material solution for hydrothermal synthesis, and forming a DDR type zeolite layer comprising a DDR type zeolite that are deposited within pores of the substrate on at least one surface thereof and having a thickness 5 to 50 times of a mean pore diameter of the porous substrate.

**Please replace the paragraph on page 50, line 19 – page 51, line 3, with the following amended paragraph:**

"Diffraction peak of a DDR type zeolite" in the X-ray diffraction is a diffraction peak described in International Center for Diffraction Data (ICDD) "Powder Diffraction File" No. 38-651 or 41-571 corresponding to Deca-Dodecasil 3R. The crystal phase of thus formed zeolite was evaluated as "amorphous" in the case that when only broad halo but no clear peak were observed, that of the one was "still under the crystallization" in the case that when even a few peaks were observed, and that of the one was "complete crystal" in the case that sharp peaks of a DDR type zeolite with no halo was observed in the x-ray diffraction in a range of 20 to 30° (CuK $\alpha$ ).—

**Please replace the paragraph on page 60, lines 2 - 25, with the following amended paragraph:**

A gas permeation test was conducted using a DDR type zeolite membrane produced in Example 1. Figure 3 schematically illustrates a configuration of a gas permeation test apparatus used in the gas permeation test, and shows a state where a shaped DDR type zeolite membrane 102 was attached to a tip of a measuring tube 101 (15 mm $\phi$  inner diameter) made of zirconia, and this was placed in a core tube 104 (25 mm $\phi$  inner diameter) of a tubular furnace 103, and a quartz tube 105 of 6 mm $\phi$  inner diameter was inserted into the measuring tube 101 to near a DDR type zeolite membrane 102 to provide a triple tube structure. Xylene containing isomers 106 of ortho, para, and meta mixed in an equimolar amount ~~was~~were introduced as a test gas via a changing valve 112 into the outside of the measuring tube 101 (inside the core tube 104) while bubbling nitrogen gas (50 ml/min) in a bubbler 111 at room temperature, and a nitrogen gas (sweep gas, 50 ml/min) for recovering a gas having permeated a DDR type zeolite membrane 102 was flown into the quartz tube 105 inside the measuring tube 101. In this state, the tubular furnace 103 was heated to a test temperature (100°C), and kept for one hour or more to reach a steady state. The

sampling gas of the recovery gas containing the gas having permeated a DDR type zeolite membrane 102 was taken, and analyzed with a gas chromatograph to evaluate a xylene gas permeance ( $\text{nmol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ ).

**Please replace the paragraph on page 63, line 15 – page 64, line 12, with the following amended paragraph:**

It can be taken, as is clear from the results shown in Tables 3, that even if the porous substrate is cylindrical, a DDR type zeolite membrane can be formed on a surface thereof. Further, it was found that a DDR type zeolite membrane has a good separation capability of a mixed gas of carbon dioxide/methane (a separation factor of carbon dioxide/methane = 90).

It was found, as is clear from the results shown in Tables 4 and Figure 4, that xylene hardly permeated a DDR type zeolite membrane, but carbon dioxide and methane permeated, and carbon dioxide showed a permeation of about 20 times higher than that of methane. This may depend on pore diameter of a DDR type zeolite membrane and a molecule diameter of the test gas.

It was found, as is clear from the results shown in Tables 5 and Figure 5, that dimethyl sulfide and tertiary butyl mercaptan having a relatively large molecule diameter, compared to methane and ethyl mercaptan having a relatively small molecule diameter, have low permeation. That is, the obtained DDR type zeolite membrane has a good separation capability of dimethyl sulfide and tertiary butyl mercaptan from methane, and thus can be used for separation of, for example, a mixed gas of dimethyl sulfide and methane, or a mixed gas of tertiary butyl mercaptan and methane.

**Please replace the paragraph on page 70, line 17 – page 71, line 6, with the following amended paragraph:**

A jar of 100 ml capacity made of fluororesin was charged with 6.01 g of ethylenediamine (produced by Wako Pure Chemical Industries, Ltd.), and then 0.95 g of 1-adamantanamine (produced by Katayama Chemical Industries Co., Ltd.) was



added and dissolved so as not to leave precipitation of 1-adamantanamine. Another beaker was charged with 43.41 g of water, and 10.01 g of 30 % by mass of silica sol (produced by Nissan Chemical Industries, Ltd., trade name: Snowtex S) ~~of were added~~ and gently stirred, and then added to the jar containing mixed ethylenediamine and 1-adamantanamine, and the resultant was vigorously shaken to prepare a raw material solution. At this time, the mixing ratio of 1-adamantanamine to silica (1-adamantanamine (mol)/SiO<sub>2</sub> (mol)) was 0.125, the mixing ratio of water to silica (water (mol)/SiO<sub>2</sub> (mol)) was 56, and the mixing ratio of ethylenediamine to 1-adamantanamine (ethylenediamine (mol)/1-adamantanamine (mol)) was 16.

**Please replace the paragraph on page 73, lines 5-26, with the following amended paragraph:**

The formation of a DDR type zeolite membranes composite was preformed by repeating operations similar to those of Example 38 except that composition ratios of the raw material solution, amounts of the raw material solution, heat treatment conditions, and shapes of the porous substrate were altered. A porous substrate in the form of a disk used in Example 38 and a porous substrate machined to be a tube of 17 mmφ outer diameter × 2.5 mm thickness were prepared as a porous substrate. The formed DDR type zeolite membrane was evaluated by X-ray diffraction the same as in Example 38, and the thickness of a DDR type zeolite layer deposited within pores of substrate and the thickness of a DDR type zeolite layer deposited outside of the substrate were measured by observation with an electron microscope. The composition ratios of the raw material solution (1-adamantanamine (mol)/silica (mol), ethylenediamine (mol)/silica (mol), and ethylenediamine (mol)/1-adamantanamine (mol)), the substrate shapes, the heat treatment conditions (temperature, time), and the thicknesses of the formed DDR type zeolite layer deposited outside of the substrate, and the thicknesses of a DDR type zeolite layer deposited within pores of substrate are shown in Table 10.

**Please replace the paragraphs on page 76, line 13 – page 77, line 11, with the following amended paragraph:**

As is clear from the results shown in Table 10, one may form a DDR type zeolite membrane composite comprising a DDR type zeolite layer deposited within pores of substrate having a thickness 5 times ( $3\text{ }\mu\text{m}$ ) or more of the mean pore diameter ( $0.6\text{ }\mu\text{m}$ ) of the porous substrate used in this embodiments, a  $\text{CO}_2/\text{CH}_4$  separation factor of 2 or more at  $100^\circ\text{C}$ , and usable as a gas separation membrane by adjusting the mixing ratio of 1-adamantanamine to silica within 0.03 to 0.5, the mixing ratio of ethylenediamine to 1-adamantanamine within 5 to 32, and the mixing ratio of water to silica within 20 to 500 (Examples 38 to 48).

It was confirmed, as is clear from the results shown in Table 10, that a DDR type zeolite membrane composite having the DDR type zeolite layer deposited within pores of substrate of  $3\text{ }\mu\text{m}$  thickness or more, and the  $\text{CO}_2/\text{CH}_4$  separation factor ~~separation factor~~ of 2 or more at  $100^\circ\text{C}$ , especially, a DDR type zeolite membrane composite having the DDR type zeolite layer deposited within pores of substrate of  $5\text{ }\mu\text{m}$  thickness or more, and a  $\text{CO}_2/\text{CH}_4$  separation factor of 50 or more at  $100^\circ\text{C}$ , can be satisfactorily used as a gas separation membrane (Examples 38, 39, 43 to 46). A permeation speed of molecules becomes lower as the DDR type zeolite layer deposited within pores of substrate becomes thicker, thus the thickness of the DDR type zeolite layer deposited within pores of substrate is preferably within 3 to  $6\text{ }\mu\text{m}$  when the porous substrate having the mean pore diameter of  $0.6\text{ }\mu\text{m}$  is used.